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The relationship between corrosion and the biological sulfur cycle

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INTRODUCTION

Most microbiologically influenced corrosion (MIC) takes place in the presence of microbial consortia in which many different physiological types of bacteria interact in complex ways within the structure of biofilms. Microbiologically-mediated oxidation and reduction reactions of sulfur and sulfur compounds are important contributors to MIC. Sulfur and sulfur compounds, including sulfides, bisulfides, hydrogen sulfide (H_2S), thiosulfates, polythionates and sulfuric acid, may be trapped or bound up in biofilms causing direct corrosion of materials. H_2S and sulfuric acid may become gaseous or waterborne.

SULFUR, SULFATE AND THIOSULFATE REDUCTION

Reduction of elemental sulfur or thiosulfate results in production of H_2S. H_2S acidifies a corrosive medium and catalyses the penetration of hydrogen into steels, a process known as H_2S-induced cracking or sulfide stress cracking. Crolet and Magot[1] described a group of bacteria isolated from an oilfield production facility capable of reducing thiosulfate ($S_2O_3^-$), not sulfate, to sulfide. Corrosion penetration rates of carbon steel in the presence of these organisms was in excess of 1 cm per year. Sulfate-reducing bacteria (SRB) can stimulate corrosion by producing sulfide minerals. McNeil and Odom[2] developed a thermodynamic model to predict metal susceptibility to MIC by SRB. Some metal oxides can be destabilized and act as a source of metal ions to react with the sulfide. The model is limited to thermodynamic predictions as to whether or not a reaction will take place and does not consider metal toxicity to the organisms, tenacity of the resulting sulfide or others factors that influence corrosion rate.

Reviews by Miller and Tiller[3], Iverson[4] and Postgate[5] provide examples and details of MIC of iron and mild steel under anaerobic conditions caused by SRB. MIC failures have been reported for mild steel piping and equipment exposed in the marine environment, soil, oil refining industry, fossil fuel and nuclear power plants and process industries.

The impact of oxygen on obligate anaerobic SRB was examined by Hardy and Brown[6] using mild steel and weight loss measurements. Successive aeration-deaeration shifts caused variation in the corrosion rate. The highest corrosion rates were observed during periods of aeration. Lee et al.[7,8] determined that corrosion of mild steel could not be initiated by SRB in the absence of ferrous ions. In their experiments, there was no correlation between corrosion rates and SRB in the absence of ferrous ions. The impact of biogenic sulfides on the corrosion of copper alloys has received a considerable amount of attention.[9,10,11]

Several investigators have demonstrated that there is no direct correlation between numbers of sulfate-reducing bacteria and the likelihood that corrosion has occurred

or will occur.[12,13] Jack et al.[12] prepared a review of 30 months of electrochemical, weight-loss data, water chemistry and microbiological data for an oilfield waterflood operation in which produced brine was injected to displace oil from the reservoir. They concluded that SRB numbers could be used as an index of biocide performance in these field systems. No other correlations between corrosion measurements and microbial numbers were found.

SULFUR/SULFIDE OXIDATION

Corrosion associated with sulfur oxidation reactions involves autotrophic organisms. Elemental sulfur, thiosulfates, metal sulfides, H_2S, and tetrathionates can be oxidized to sulfuric acid. The specific oxidation reactions leading to production of sulfuric acid varies with the starting reduced sulfur species.

Corrosion in sewers and other concrete structures is often due to the oxidation of sulfides generated by the activities of SRB and may occur in many steps. Concrete is a moderately porous mixture of highly alkaline inorganic precipitates and mineral aggregate. Strong acids react with concrete materials destroying its structural integrity. Anaerobic conditions in sewage support SRB that convert sulfate and organic sulfides to H_2S, which volatilizes to the sewer atmosphere and redissolves in condensate on the sewer crown. A second community of microorganisms, including *Thiobacilli*, at the crown oxidizes the sulfide to corrosive sulfuric acid. Mittleman and Danko[14] determined that similar cycling of sulfur, i.e., sulfate reduction and sulfide oxidation, by microorganisms was responsible for concrete and carbon steel deterioration in a dam in South America.

Sulfide oxidation reactions are important to the formation of sulfuric acid in coal mines and in sulfur deposits. If FeS_2 containing coals are exposed to moisture and oxygen, spontaneous FeS_2 oxidation starts, resulting in production of ferric iron and sulfuric acid. The pH of the water phase will drop during the oxidation process. Acidophilic pyrite oxidizing bacteria, indigenous in coals, thrive at low pH and continue the oxidation to pH values lower than 2. The ferric iron produced in these reactions acts as an oxidizing agent to solublize other metal sulfides. Reviews on pyrite oxidation have been published by Lowson,[15] Nordstrom,[16] and Evangelou.[17] The South African Rail Company, a carrier for large quantities of low-grade coal, reported accelerated corrosion of 3Cr12 steel due to the presence and activities of *T. ferrooxidans* and the fungus, *Hormoconis resinae*. The individual organisms caused an approximate doubling of the corrosion rate compared to sterile conditions. The corrosion pattern included scaling, pitting, and stress-cracking.[18] Similar situations are found where pipelines are buried in soils that contain coal ash, industrial wastes, landfills or railway right-of-ways through coal outcroppings and rivers in the coal mining regions.

CONCLUSION

Sulfur and sulfur compounds can produce pitting, crevice corrosion, dealloying, stress corrosion cracking and stress-oriented hydrogen induced cracking of susceptible metals and alloys. Determination of specific mechanisms for corrosion due to microbiologically mediated oxidation and reduction of sulfur and sulfur compounds is complicated by (1) the variety of potential metabolic/energy sources and by-products (2) the coexistence of reduced and oxidized sulfur species (3) competing reactions with inorganic and organic compounds, and (4) the versatility

and adaptability of microorganisms in biofilms. The microbial ecology of sulfur-rich environments is poorly understood because of the association of aerobes and anaerobes and the mutualism or succession of heterotrophs to autotrophs. The physical scale over which the sulfur cycle influences corrosion varies with the type environment. The complete sulfur cycle of oxidation and reduction can take place in macroenvironments, including sewers and polluted harbors or within the microenvironment of biofilms in process equipment.

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